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### Surface Site Preferences for Cu(II) Uptake by Calcite

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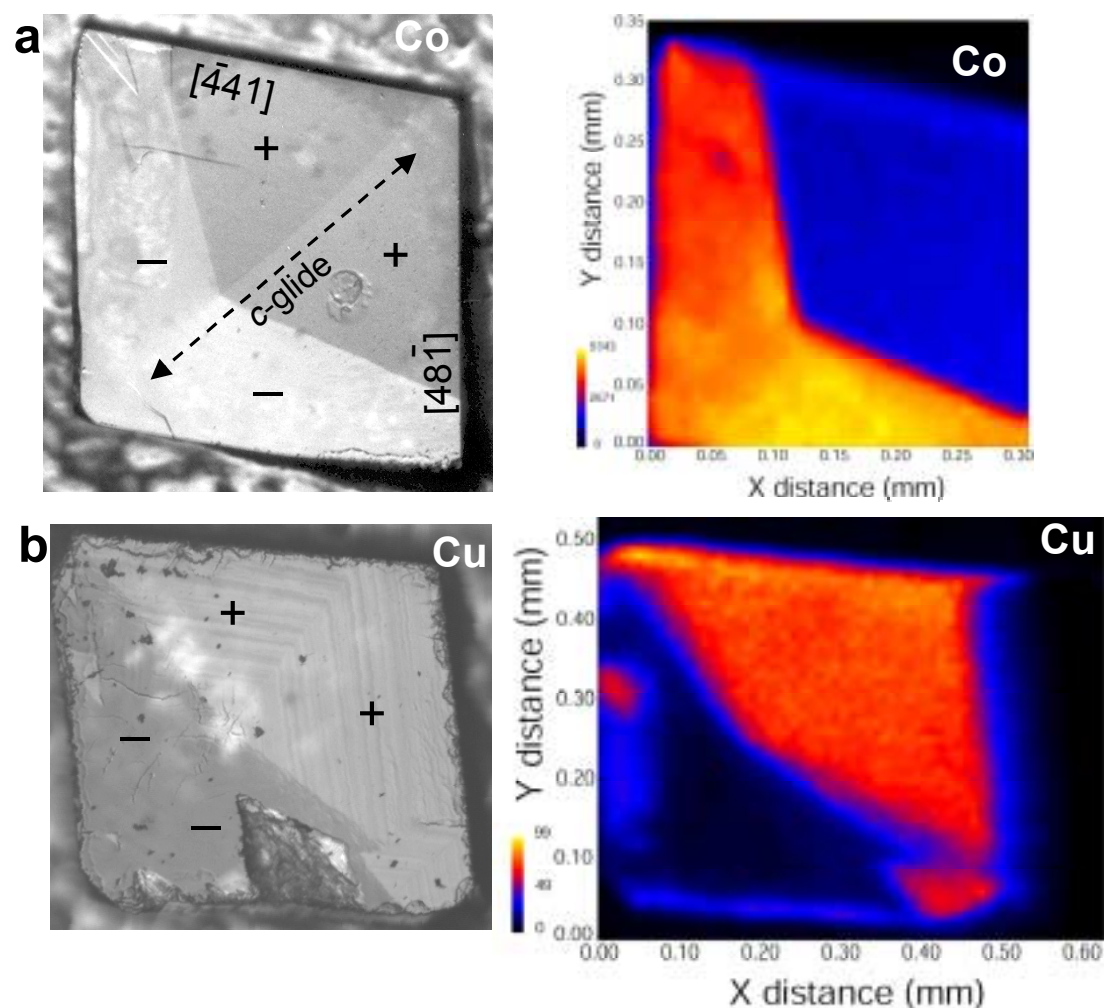
Beamline(s): X26A

**Introduction:** Uptake of divalent metals during coprecipitation with calcite ( $\text{CaCO}_3$ ) is known to result in heterogeneous incorporation on the (10.4) growth face due to the presence of multiple surface sites. Polygonized growth spirals result in two pairs of equivalent vicinal surfaces (labeled “+” and “-” in figure), each having growth steps with distinct incorporation sites. However, “+” and “-” steps are nonequivalent, resulting in differential metal uptake during growth. Here, we compare the site preference for Cu(II) with previous work for Co(II).

**Methods and Materials:** Calcite single crystals were synthesized from room-temperature solutions containing Co(II) or Cu(II). Thin sections of the crystals containing the (10.4) growth face were mounted on high-purity glass disks. Micro-X-ray fluorescence mapping was conducted at beamline X26A using a  $12 \times 14 \mu\text{m}$  monochromatic beam and a Si(Li) detector.

**Results:** Both Co(II) and Cu(II) are differentially incorporated between the nonequivalent vicinals as shown by the close correspondence between the different vicinal faces and the Co or Cu concentrations (see figure). However, the metals show opposite preferences, with Co(II) preferring the “-” surfaces and Cu(II) the “+” surfaces. Related EXAFS work shows that a Jahn-Teller distortion of octahedral Cu(II) sorption complexes is most likely responsible for the different surface site preferences.

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Differential interference contrast (DIC) images of as-grown (10.4) calcite surfaces (left) and corresponding micro-X-ray fluorescence maps (right) for Co(II)-doped (top) and Cu(II)-doped (bottom) calcite. Yellow-red areas in X-ray maps indicate highest metal concentrations.